THE RELATIONSHIP BETWEEN THE CONSISTENCY OF THE GREEN ELECTRODE MIX AND THE PROPERTIES OF TEST ELECTRODES

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Introduction

In the panel discussion that followed the symposium on "Tars, Pitches and Asphalts" at the 1959 spring meeting of the American Chemical Society in Boston, members of the panel emphasized that more attention should be given to the measurement and study of the rheological properties of green electrode mixes.

Because of widespread interest in this subject, a preliminary research program was initiated at the Applied Research Laboratory of the United States Steel Corporation to investigate the relationship between the consistency of the green mix and the crushing strength and volume electrical resistivity of specimen electrodes. Consistency has been defined as that property of a body that tends to resist deformation.[1)]* In this paper, consistency is defined more specifically as the torque required to shear the green mix at a constant rate and temperature.

A careful search of the Chemical Abstract indexes covering a 53-year period from 1907 to 1960 revealed that no information has been published on the relationship between the consistency of the green mix and the properties of test electrodes. Only one reference[2)] was found that described an instrument for quantitatively measuring the consistency of green electrode mixes. This instrument, Russian-built, is simply a cone penetrometer that has been modified to measure the pressure (limiting shear stress) required to drive a standard cone, under constant force, into the test mixture to a full stop. Although this instrument has many desirable features, such as simplicity of design and operation, it was not precise or sensitive enough for use in the present investigation. Subsequently, a technical brochure[3)] indicated that another instrument, the Brabender Plastograph, had the desirable characteristics, and was used in the ensuing investigation.

This paper describes the evaluation of rheological properties of green mixes prepared from two coal-tar pitch binders and the properties of the test electrodes made from them. It is hoped that this information will provide a better understanding of the relationship between the rheology of the green mix and electrode performance.

Experimental

For this preliminary study two electrode binders and a calcined petroleum coke were used. The more common properties of the binders are shown in Table I. Both binders were produced in full-scale equipment from the same feed stock. Binder A, a pitch of demonstrated utility, was produced by continuous vacuum-flash distillation. Binder B was specially processed to have essentially the same softening point as Binder A, but a viscosity and a β-resin content significantly higher.

With the exception of the viscosity, standard test methods common to the aluminum and carbon industries were used to measure the properties of the binders. The absolute viscosity of the binders was determined by a Brookfield Synchro-Lectric Viscometer equipped with a 12-inch spindle extension. A special device for heating

* See References.

the air in contact with the pitch and the spindle was used with this instrument. A schematic drawing of the assembled apparatus is shown in Figure 1. The air heater was used to reduce the unwanted drag or torque exerted on the rotating spindle by the "skin" of pitch that has a tendency to form on the surface of the test sample when it is exposed to air at room temperature.

Selected properties of the petroleum coke, used by the Laboratory as a standard, are shown in Table II. The coke was calcined at 1300 C by the supplier and then graded at the Laboratory into the six fractions shown in the table. Because the fractions were sized relative to the dimensions of our laboratory-scale electrode-baking apparatus, they are smaller than the fractions used commercially.

Since the experimental procedures are somewhat involved, the major steps are briefly outlined below. A more detailed discussion of the various procedures will follow.

1. A series of green mixes containing from 31 per cent to 38 per cent binder was prepared in a Brabender Plastograph.

2. The consistency of each mix was measured in the Plastograph as the mix was being prepared.

3. Each batch of green mix was then baked in accordance with a standard Laboratory procedure to yield small test electrodes.

4. The electrodes were tested for crushing strength and volume electrical resistivity.

The Brabender Plastograph, used to prepare the green mixes and measure their consistencies, is shown in Figure 2. The instrument was purchased from C. W. Brabender Instruments Inc., South Hackensack, New Jersey. The sigma blades in the mixing head (1) are driven by a dynamometer (2), which is suspended between floating bearings (3). The torque produced by the blades as they turn in the material at a constant rate of shear is transmitted to the dynamometer. The dynamometer translates the torque through a series of balance levers (4) to a direct-reading balance (5), which is calibrated to indicate the torque in meter-gram units. A strip chart (6) provides a continuous record of the consistency in terms of meter-gram units. Excessive movement of the lever system is dampened by an oil dash pot (7).

The mixing head has a working capacity of 650 milliliters. It is heated by recirculating hot oil from a constant-temperature bath (8) through a jacket that surrounds the mixing head. A special insulated lid (9), not supplied by the manufacturer of the instrument, minimizes the loss of heat from the head and was indispensable as an aid in maintaining the mix at a uniform temperature. Through a small opening in the lid, 5/8 inch in diameter, coke additions can be made without removing the lid.

As mentioned above, green mixes containing from 31 per cent to 38 per cent binder were prepared and their consistencies measured. The composition of a typical batch of green mix is shown in Table III. In this batch, 462 grams of the various coke fractions were blended, as described below, with 238.0 grams (34 weight per cent) of Binder A to yield 700 grams of mix. In all the mixes, the total amount of the two components was held constant at 700 grams.

In the preparation of a typical mix, the calculated amount of molten binder, at a temperature of about 155 C, is added to the preheated mixing head. After the binder has mixed for exactly 7 minutes, the preheated (to 155 C) 10- to 30-mesh coke

fraction is added through the opening in the insulated lid. The remaining fractions are then added in the order of decreasing size at 5-minute intervals. The addition of these fractions is illustrated in Figure 3. Mixing is continued at 155 C for 30 minutes after the addition of the last (minus 325-mesh) coke fraction. The torque reading, in meter-grams, at the end of this mixing period is recorded as the consistency of the mix.

The change in consistency that occurs as the various coke fractions are added to the binder is illustrated by the typical consistency curves that are reproduced in Figure 4. Reading from right to left, the steps in the curve represent the increase in consistency that occurs as the six coke fractions are added to the binder at 5-minute intervals. The position of the left extremity of the curve defines the consistency of the mix. The sensitivity of the instrument to the change in consistency brought about by the addition of the various coke fractions is clearly indicated. The second curve in this figure was included to demonstrate the excellent repeatability of the instrument over the entire consistency range.

After measuring the consistency, the green mixes were packed into perforated graphite molds, Figure 5, and baked to a temperature of 1000 C in 24 hours. The baked electrodes were then tested for crushing strength and electrical resistivity. The procedure for preparing, baking, and testing specimen electrodes was described in a paper[4] presented at the Spring 1959 meeting of this Division.

Results and Discussion

To make clear the relationship between the consistency of the various green mixes and the properties of the test electrodes, the experimental data were plotted in bar-chart form. The relationship between the consistency and crushing strength for both binders is illustrated in Figure 6. The black bars represent the consistency of the mix at various levels of binder concentration, and the white bars show the crushing strength of specimen electrodes prepared from green mixes containing various percentages of binder. The number at the top of each bar represents the percentage of binder in the mix. From this chart, it is evident that an excellent correlation exists between the consistency of the green mix and the crushing strength of the test electrodes. It is extremely interesting to observe that, as the percentage of binder increases within the limits shown, the consistency and crushing-strength values for each binder pass through a maximum simultaneously. This relationship suggests that the consistency of a green mix can be measured to determine the optimum percentage of binder to use in the preparation of an electrode with maximum crushing strength. For Binder A, for example, a maximum consistency value was obtained at a binder concentration of 34 per cent. This mix in turn produced an electrode with the highest strength. Therefore, the optimum percentage of binder is 34 per cent.

This chart also shows that Binder B, which had been processed to have a higher viscosity than A, yielded mixes with consistencies significantly higher than those of Binder A. In a like manner, Binder B produced electrodes with crushing strengths somewhat higher than those of Binder A. It is also interesting to note that the percentage of binder required to obtain electrodes with maximum strength was about the same for each binder. The fact that a stronger electrode can be obtained with the specially treated binder (Binder B) seems to indicate that the special treatment was indeed very beneficial.

Figure 7 shows the relationship between the consistency of the mix and the electrical resistivity of the electrodes. It is evident that a good correlation also exists between these parameters. For each binder, as the consistency values pass through a maximum the resistivity values pass through a minimum. This relationship

suggests that the consistency of the mix can also be employed to determine the optimum percentage of binder to use in preparing an electrode with minimum electrical resistivity. Binder B produced electrodes with resistivities somewhat lower than those of Binder A. Once again, the beneficial effect of the special treatment was demonstrated.

Summary

The Applied Research Laboratory has studied the relationship between the consistency of the green electrode mix and selected properties of test electrodes. The results of this preliminary investigation suggest that (1) the consistency of the green mix can be used to determine the optimum concentration of binder required to produce electrodes of the highest quality, (2) the Brabender Plastograph, with slight but important modifications, is a suitable instrument for measuring the consistency of green mixes, and (3) for the same concentration of binder in the green mix, an appropriately treated binder will yeild better electrodes than an untreated binder. This investigation is being continued to further verify and extend these findings. It is anticipated that the results of this more extensive study will be presented at a future meeting of this Division.

Literature References

1. "Standard Definitions of Terms Relating to Rheological Properties of Matter," ASTM Standards 1942, I, 941.

2. A. S. Fialkov and I. G. Davidovitch, "The Use of a Conical Plastometer for Controlling the Quality of Mixtures of Carbon Compositions," Zavodskaya Laboratoriya (USSR), 9, 261 to 263 (1957).

3. Technical Brochure, Brabender Plastograph, C. W. Brabender Instruments Incorporated, South Hackensack, New Jersey.

4. H. L. Jones, Jr., A. W. Simon, and M. H. Wilt, "A Laboratory Evaluation of Pitch Binders Using Compressive Strength of Test Electrodes," Journal of Chemical and Engineering Data, 5, No. 1, 84 to 87 (1960).

Table I

PROPERTIES OF BINDERS

	BINDER A	BINDER B
SOFTENING POINT, CUBE-IN-AIR, C	102.3	105.5
BETA RESINS (BI-QI), wt %	11.9	19.2
SPECIFIC GRAVITY (60 F/60 F)	1.32	1.32
VISCOSITY, CENTIPOISES		
at 140 C	4600	7610
at 150 C	1630	3200
at 160 C	810	1340
IRON, wt %	0.020	0.018
ATOMIC CARBON/HYDROGEN RATIO	1.78	1.77
BENZENE INSOLUBLES, wt %	21.9	28.6
QUINOLINE INSOLUBLES, wt %	10.0	9.4
COKE VALUE, CONRADSON, wt %	55.2	55.4
DISTILLATION, wt %		
to 270 C	0.0	0.0
270 to 300 C	0.2	0.2
300 to 360 C	1.7	2.6
360 to 400 C	10.1	10.1
SULFUR, wt %	0.62	0.59

Table II

PROPERTIES OF CALCINED PETROLEUM COKE

APPARENT DENSITY, GM/CM^3	0.898
CARBON, wt%	97.61
HYDROGEN, wt%	0.24
ASH, wt %	0.35
SULFUR, wt%	1.27
SIEVE ANALYSIS, wt %	
-10 +30 MESH	20
-30 +50 MESH	16
-50 +100 MESH	19
-100 +200 MESH	13
-200 +325 MESH	10
-325 ON PAN	22

Table III

COMPOSITION OF A TYPICAL BATCH OF GREEN MIX

	WEIGHT IN GRAMS	WEIGHT PER CENT OF MIX
BINDER A	238.0	34.0
COKE FRACTIONS		
-10 +30 MESH	92.4	13.2
-30 +50 MESH	73.9	10.6
-50 +100 MESH	87.8	12.5
-100 +200 MESH	60.1	8.6
-200 +325 MESH	46.2	6.6
-325 ON PAN	101.6	14.5
TOTAL	700.0	100.0

Note: Coke fractions are added to the binder in the order of decreasing particle size.

APPARATUS FOR VISCOSITY DETERMINATIONS

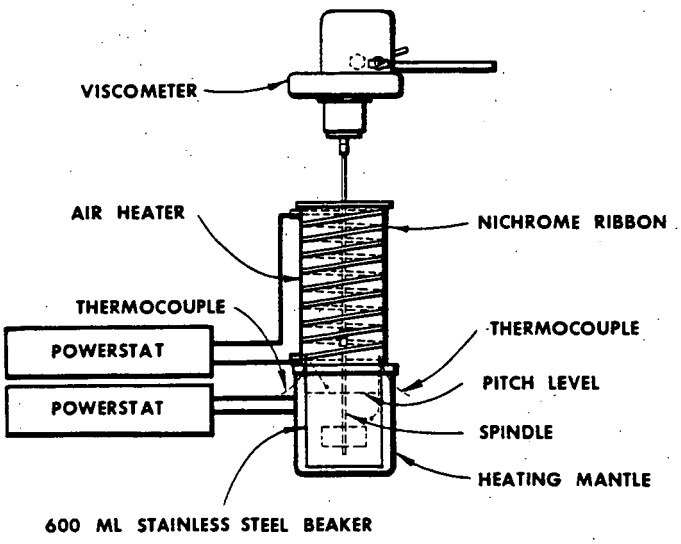

Figure 1. APPARATUS FOR VISCOSITY DETERMINATIONS

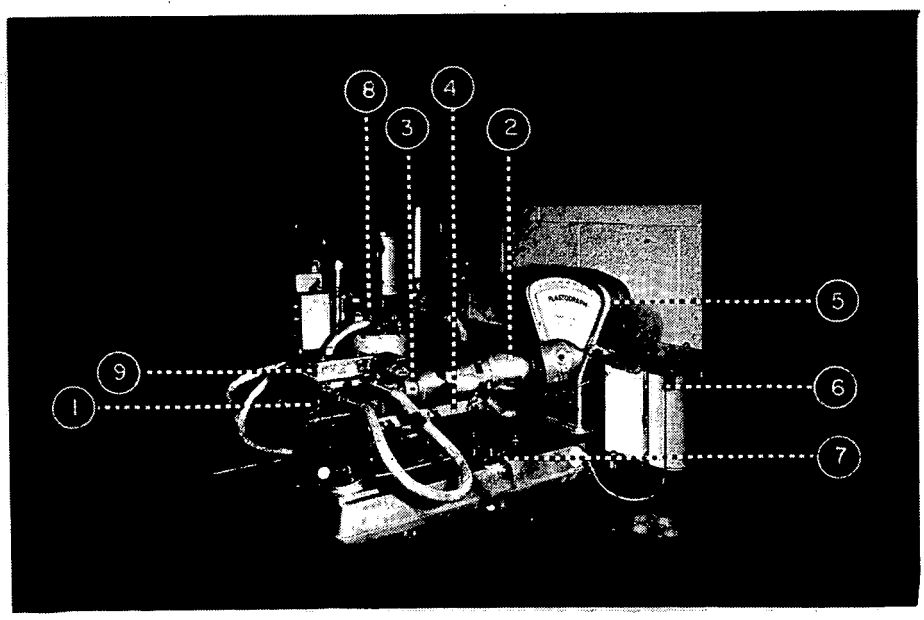

Figure 2. BRABENDER PLASTOGRAPH

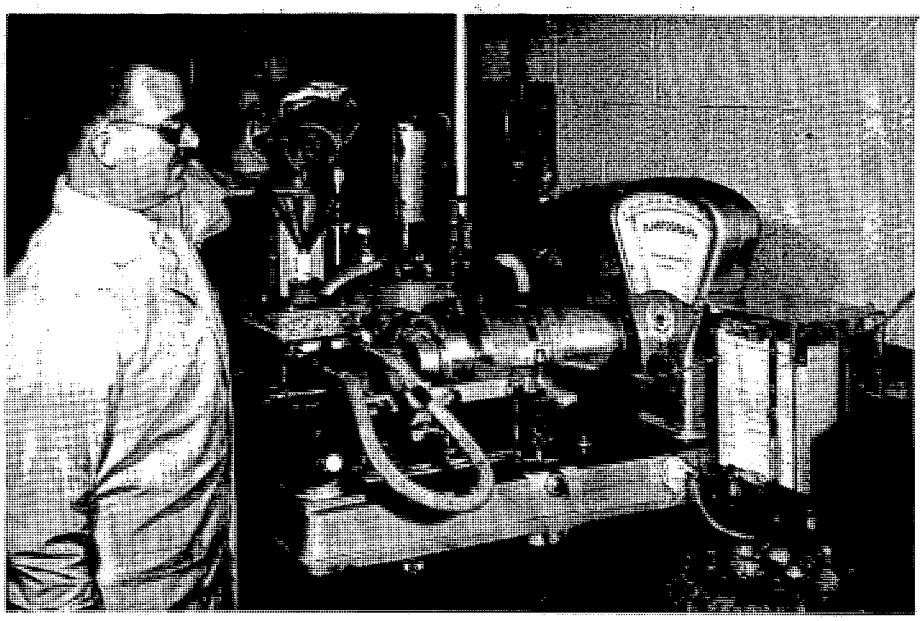

Figure 3. ADDING PETROLEUM COKE FRACTIONS

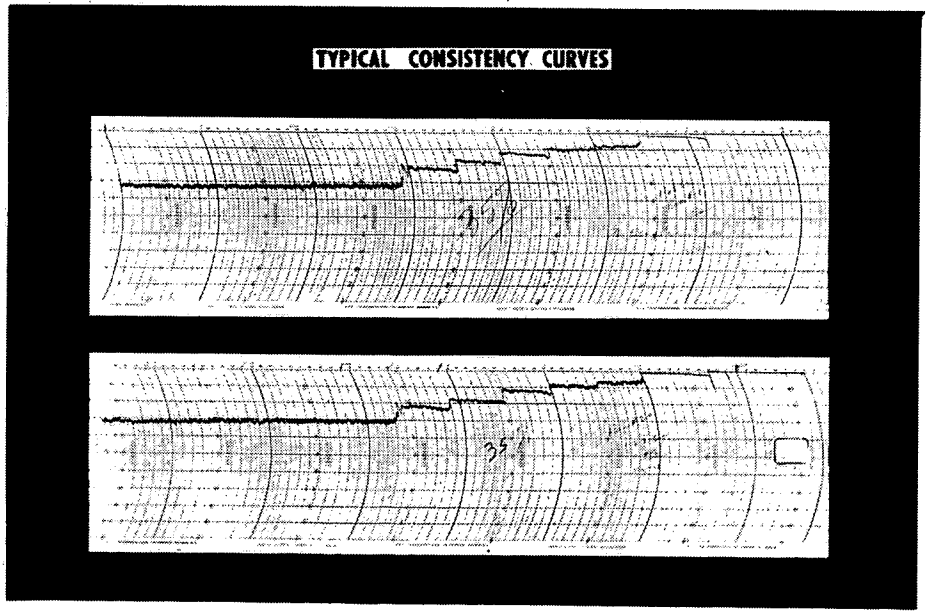

Figure 4. TYPICAL CONSISTENCY CURVES

Figure 5. PACKING THE GREEN MIX

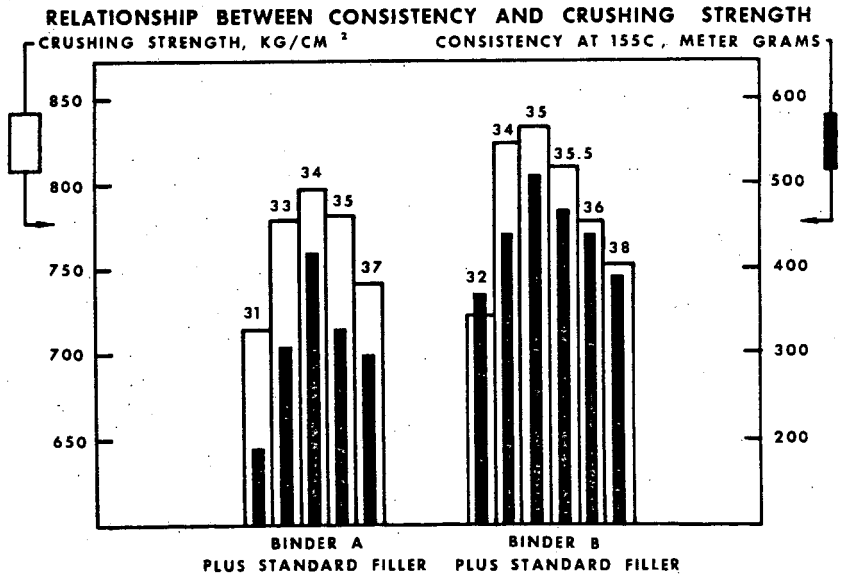

Figure 6. RELATIONSHIP BETWEEN CONSISTENCY AND CRUSHING STRENGTH

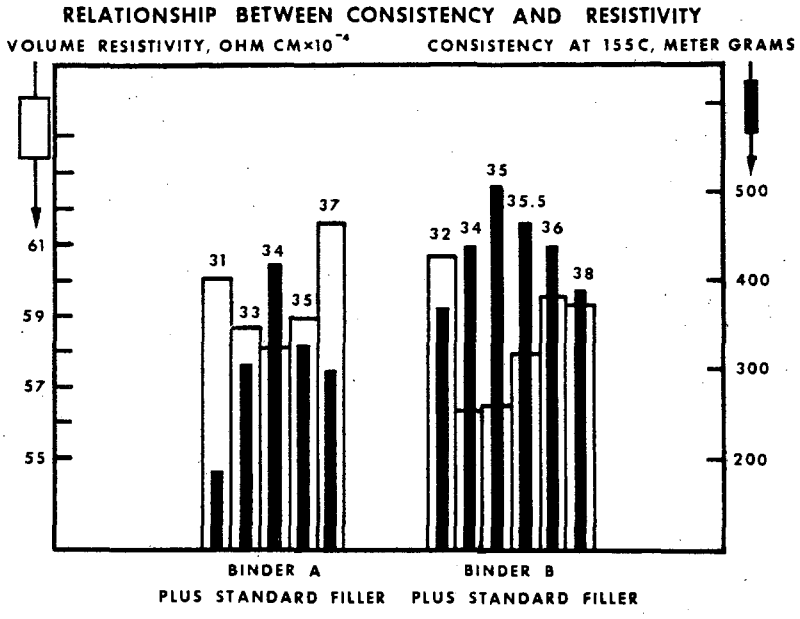

Figure 7. RELATIONSHIP BETWEEN CONSISTENCY AND RESISTIVITY